

Melt Flow Index Values and Molecular Weight Distributions of Commercial Thermoplastics

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Synopsis

The traditional melt index test (ASTM D 1238) is widely used in the plastics industry to characterize polymer processability. The data from this measurement must be interpreted cautiously, however, because polymers are usually processed under conditions that are far removed from those of the melt index test. In this study, melt index (MI) values from a series of polystyrene, polypropylene, linear low-density polyethylenes (butene and octene copolymers), and high-density polyethylenes were measured and related to molecular weight distributions of these materials. It was found that a simple relationship between $1/MI$ versus M_w^α (where $\alpha = 3.4-3.7$) was followed for the linear polymers with similar polydispersities. For branched polymers, the best correlation was that of $-\ln(MI)$ versus $\ln(\bar{M}_w)$. A general relation for shear modifiable polymers like polyethylenes cannot be obtained unless the rheological state of the material can also be defined.

INTRODUCTION

To the best of our knowledge, the melt flow index measurement was invented by W. G. Oakes at ICI, in England, in the early days of polyethylene production. The original intention was to provide a convenient index of processability and product quality control. The method is now used for these purposes with a wide variety of thermoplastics. The procedure is described in ASTM test method D 1238-82 "Flow Rates of Thermoplastics by Extrusion Plastomer."¹ It comprises measurement of the mass flow rate of a polymer through an orifice of specified dimensions under prescribed conditions of load, temperature, and position of a driving piston in the plastometer barrel. The weight of a 10-min extrudate is the melt index (or melt flow index, MFI) of the polymer.

The data produced by this technique must be interpreted cautiously because the method suffers from several severe shortcomings. First, the flow rates that are measured are not always steady-state values.² The actual results may be very sensitive to the details of the measurement procedure, especially for low melt index polymers. Second, and more important, melt index values cannot be expected to be very useful predictors of processability since most commercial thermoplastics are shear thinning and are actually processed at much higher shear rates than those that prevail during the melt index measurement.

These inherent problems are widely known but little appreciated, even though the melt flow index measurement is deeply embedded in modern plastics tech-

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nology. Variations of the procedure have been devised for different polymers and processability ranges,¹ and it is practically impossible to produce or select polyolefins, styrenics, and other materials without specifying the melt index of the product. Thus, it would be beneficial to be able to relate the melt index of a polymer to some characteristics of its molecular weight distribution (MWD) since the latter is presumably the unifying factor whereby relations can be established between polymerization conditions on the one hand and product properties on the other.

The method of current choice for characterizing MWD is size exclusion chromatography (SEC). There are reports that rheological properties of polymer melts have a common dependence on MWD.² Some authors have in fact reversed the process and attempted to deduce MWDs from measurements of rheological behavior.^{4,5} With this recent background, it seems worthwhile to examine the relation between MWD data and melt index for several important polymer types.

We show that a very simple correlation does exist for the commercial range of crystal polystyrenes and isotactic polypropylenes. The same relation has some real value in the case of polyethylenes, but its value here is limited because long and short chain branching may be a function of molecular weight,⁶ and the melt indices of these polymers may also be affected by shear and thermal history effects.⁷

EXPERIMENTAL

The polymers examined in this study include:

- Six commercial polystyrenes, crystal grade, that were free of oils or other processing aids, with MI values between 4.6 and 40
- Five commercial polypropylenes with MI values between 0.7 and 12
- Ten LLDPE ethylene-butene copolymers made by the Unipol process, with MIs between 0.3 and 100
- Six HDPE polymers made by a slurry process, with MI values between 0.14 and 6.2
- Six LLDPE octene-ethylene copolymers made by the Dowlex process, with a narrow MI range of 0.8-1.4.

Table I lists \bar{M}_n , \bar{M}_w , \bar{M}_z , and \bar{M}_z values of all the polymers tested. All polymers were used as received from the manufacturers.

Molecular weight distributions were measured by SEC, using differential refractive index and low-angle laser light scattering (LALLS) detectors. Universal calibration was with narrow distribution polystyrenes. The solvent used was 1,2,4-trichlorobenzene at 145°C. Full operating procedures have been described elsewhere.^{8,9}

The LALLS detector is very sensitive to high molecular weight species and insensitive to smaller macromolecules. (The LALLS measures turbidity, which depends on the product of molecular size and concentration.¹⁰) By contrast, the differential refractometer (DRI) responds more strongly to lower molecular

TABLE I
 Molecular Weights of Polymers Used

| Sample | MFI | \bar{M}_n | \bar{M}_w | \bar{M}_z | \bar{M}_v |
|-----------------------------------|-------|-------------|-------------|-------------|-------------|
| <i>Polystyrene</i> | | | | | |
| 1 | 4.6 | 133000 | 214000 | 336000 | 521000 |
| 2 | 11.9 | 107000 | 167000 | 262000 | 424000 |
| 3 | 14.7 | 86000 | 134000 | 242000 | 408000 |
| 4 | 25.0 | 84000 | 137000 | 210000 | 325000 |
| 5 | 26.3 | 74000 | 135000 | 202000 | 323000 |
| 6 | 39.3 | 86000 | 139000 | 201000 | 350000 |
| <i>Polypropylene</i> | | | | | |
| 1 | 0.63 | 44900 | | 646000 | 2740000 |
| 2 | 0.79 | 39800 | | 567000 | 2150000 |
| 3 | 2.9 | 28000 | | 412000 | 2000000 |
| 4 | 4.7 | 25000 | | 381000 | 2220000 |
| 5 | 11.9 | 11600 | | 297000 | 2010000 |
| <i>LLDPE (1-butene comonomer)</i> | | | | | |
| 1 | 0.3 | 10000 | 96000 | 167000 | 416000 |
| 2 | 0.6 | 9000 | 80000 | 103000 | 498000 |
| 3 | 1.0 | 20000 | 78000 | 145000 | 1106000 |
| 4 | 0.8 | 10000 | 76000 | 131000 | 456000 |
| 5 | 1.2 | 15000 | 75000 | 68000 | 201000 |
| 6 | 4.0 | 17000 | 65000 | 79000 | 460000 |
| 7 | 2.0 | 10000 | 63000 | 102000 | 454000 |
| 8 | 20 | 11000 | 43000 | 54000 | 167000 |
| 9 | 50 | 13000 | 42000 | 48000 | 193000 |
| 10 | 100 | 6000 | 23000 | 38000 | 439000 |
| <i>LLDPE (1-octene comonomer)</i> | | | | | |
| 1 | 0.98 | 22000 | 82000 | 154000 | 366000 |
| 2 | 0.83 | 24000 | 74000 | 158000 | 350000 |
| 3 | 0.013 | 21000 | 71000 | 178000 | 369000 |
| 4 | 0.97 | 22000 | 68000 | 158000 | 327000 |
| 5 | 0.87 | 23000 | 66000 | 151000 | 359000 |
| 6 | 1.4 | 23000 | 61000 | 142000 | 314000 |
| <i>HDPE</i> | | | | | |
| 1 | 6.2 | 15000 | 46000 | 147000 | 615000 |
| 2 | 6.11 | 16000 | 48000 | 143000 | 659000 |
| 3 | 0.201 | 17000 | 79000 | 295000 | 1033000 |
| 4 | 0.194 | 16000 | 84000 | 294000 | 1026000 |
| 5 | 0.143 | 17000 | 74000 | 302000 | 1030000 |
| 6 | 0.138 | 16000 | 76000 | 291000 | 1019000 |

weight species since its sensitivity is supposed to be independent of size of the dissolved molecules. The best values for \bar{M}_w and \bar{M}_z are therefore from LALLS operation, while \bar{M}_n is obtained from DRI response and the universal calibration procedures. These averages are quoted as noted from the appropriate procedures.

\bar{M}_v is derived from the universal calibration curve and therefore stems from DRI operation.

We note here for completeness that \bar{M}_v is different from the other molecular weight averages quoted in that it can be a function of the solvent used for analysis as well as of the MWD of the polymer. \bar{M}_v can be shown to be defined by

$$\bar{M}_v = [\sum w_i M_i^a]^{1/a} \quad (1)$$

where w_i is weight fraction of species with molecular weight M_i and a is the exponent in the Mark-Houwink relation:

$$[\eta] = K\bar{M}_v^a \quad (2)$$

In general, the broader the MWD, the more \bar{M}_v may vary in different solvents.¹¹ \bar{M}_v is usually close to but smaller than \bar{M}_w because \bar{M}_w is defined as

$$\bar{M}_w = \sum w_i M_i \quad (3)$$

and the exponent a in eq. (2) is usually between about 0.6 and 0.75 in solvents used for SEC analyses. For our particular solutions in TCB at 145°C, $K = 0.0121$ and $a = 0.707$ for polystyrene,¹² $K = 0.0596 \text{ cm}^3/\text{g}$ and $a = 0.69$ for polyethylene, and $K = 0.0158 \text{ cm}^3/\text{g}$ and $a = 0.75$, for polypropylene.¹³

Measurement of melt flow was carried out according to ASTM method D-1238-82. The polystyrene samples were analyzed using the condition designated 230/3.8, while the polyethylene samples were characterized using condition 190/2.16. The polypropylene samples melt flow index was measured under condition 230/2.16.

RESULTS AND DISCUSSION

The relationship between MI and molecular weight can be formulated in an approximate way. Consider a melt indexer, where a weight (constant pressure, P) is placed on a piston that forces polymer through a fixed die with radius R and length L . The melt index is given in units of grams/time. Therefore,

$$\text{Melt index} = \text{MI} = \rho \sigma Q \quad (4)$$

However, from the Poiseuille equation for flow through an orifice,

$$\text{Melt viscosity, } \eta = \frac{\pi P r^4}{8QL} \quad (5)$$

Combining (4) and (5),

$$MI = \frac{k\sigma\pi PR^4}{8\eta L}$$

or

$$MI = \frac{K}{\eta} \quad (6)$$

where σ = polymer density, g/cm³
 Q = polymer volumetric flowrate, cm³/s
 k = 600 s/(10 min)
 P = pressure, g/cm s² (dynes)
 R = die orifice radius, cm
 L = orifice length, cm
 η = melt viscosity, g/cm s (poise)
 $K = \frac{\pi h\sigma PR^4}{8\eta L}$

Note that under melt index conditions, K will be a constant for a given polymer. Many equations have been put forward for the relationship between viscosity and shear stress.¹⁴ A common form is

$$\frac{\eta_0}{\eta} = f(\tau) \quad (7)$$

where η_0 is zero shear viscosity and η is viscosity at shear stress τ . However, $\tau = RP/2L$ = a constant for a melt indexer. Therefore $f(\tau)$ in eq. (7) may be considered a constant, K' . Therefore,

$$MI = \frac{KK'}{\eta_0} \quad (8)$$

The zero shear viscosity can be related to \bar{M}_w of the polymer by

$$\eta_0 = K''\bar{M}_w^\alpha \quad (9)$$

(typically, α is from 3.4 to 3.7). Combining eqs. (8) and (9),

$$MI = \frac{KK'}{K''\bar{M}_w^\alpha}$$

or

$$MI^{-1} = G\bar{M}_w^\alpha \quad (10)$$

where

$$G = \frac{K''}{KK'}$$

Hence, the inverse of the melt index is proportional to \bar{M}_w^x . This simple result ignores variations in polydispersity that are known to cause shifts in x and also ignores changes in K'' that can result from the addition of processing oils and other materials to the polymer. Nevertheless, for polymers made by one manufacturer with a fixed additive package and uniform polydispersity, the preceding form should hold.

A plot of $1/\text{MI}$ vs. $\bar{M}_w^{3.4}$ for the polystyrene samples is shown in Figure 1; a good linear agreement is obtained. It should be noted that the samples tested had similar polydispersities (\bar{M}_w/\bar{M}_n and \bar{M}_z/\bar{M}_w) and no added processing oils. Interestingly, however, added oils can be incorporated into the melt index equation, as shown by results from Wooden and co-workers¹⁰ using a log form of eq. (10):

$$\ln(\text{MI}) = 22.15 - 3.79 \ln(\bar{M}_w) + 0.255(\text{oil}) \\ + 0.189(\text{low}) + 0.495(\text{monomer}) \quad (11)$$

where oil = mineral oil concentration
 low = low molecular weight polymer (fraction below $\bar{M}_w = 5000$)
 concentration
 monomer = styrene concentration

For the polypropylene samples, the plot of $1/\text{MI}$ vs. \bar{M}_w^x (Fig. 2) gives the best fit with $x = 3.7$. The plot of $1/\text{MI}$ vs. $\bar{M}_w^{3.4}$ for ethylene/1-butene copolymer samples (Fig. 3) does not give as good a result as for the polystyrene case. However, a plot of $1/\text{MI}$ vs. $\bar{M}_w^{3.7}$ was essentially linear, as shown in Figure 4.

The plot for ethylene/1-octene copolymers is shown in Figure 5. The spread of melt indices is not very great, but it appears that a linear relationship can be seen. At the same time, however, one sample is far removed from the others.

The data for the HDPE samples are plotted in Figure 6. The correlation is quite poor and may reflect the problems of getting reliable low melt indices, as well as the effects of prior shear history on the melt flow properties of such polymers.^{2,16}

Since the molecular weight distributions of all polystyrene samples are similar, it is not surprising that good correlation is seen between the logarithm of the MFI and any molecular weight average. Practically, the most accessible molecular weight average is \bar{M}_v , from dilute solution viscometry. A plot of $\ln \text{MFI}$ vs. \bar{M}_v for these polymers is shown in Figure 7. The correlation coefficient for this linear least squares fit is 0.93. The relation between MFI and \bar{M}_v can be attributed to the parallels between \bar{M}_v and \bar{M}_w already noted.

The best statistical correlation for the ethylene/1-butene copolymers exists between $\ln \text{MFI}$ and \bar{M}_v . The linear equation relating these two parameters is

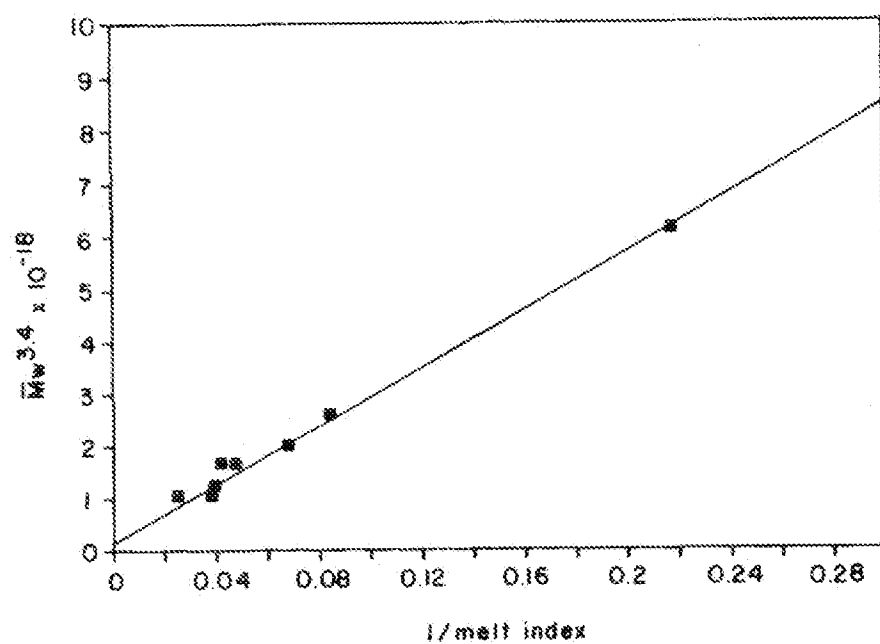


Fig. 1. Inverse melt flow index vs. \bar{M}_w^{24} for polystyrene samples.

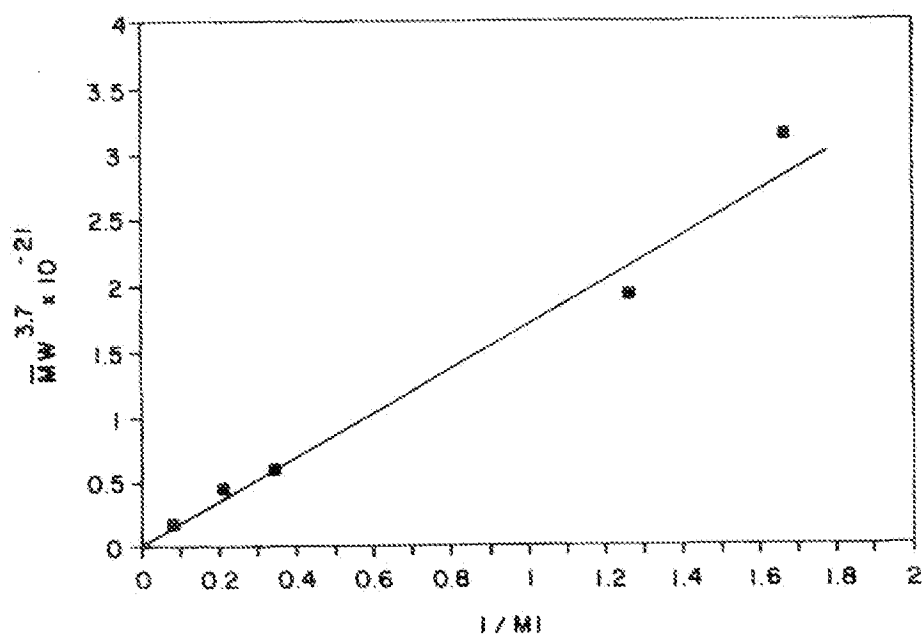


Fig. 2. Inverse melt flow index vs. \bar{M}_w^{27} for polypropylene samples.

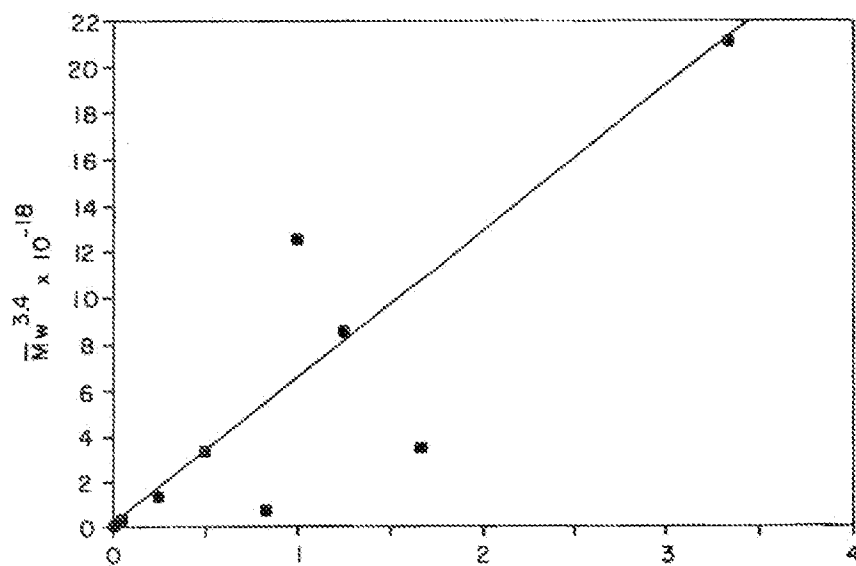


Fig. 3. Inverse melt flow index vs. $M_w^{0.34}$ for ethylene/1-butene copolymers.

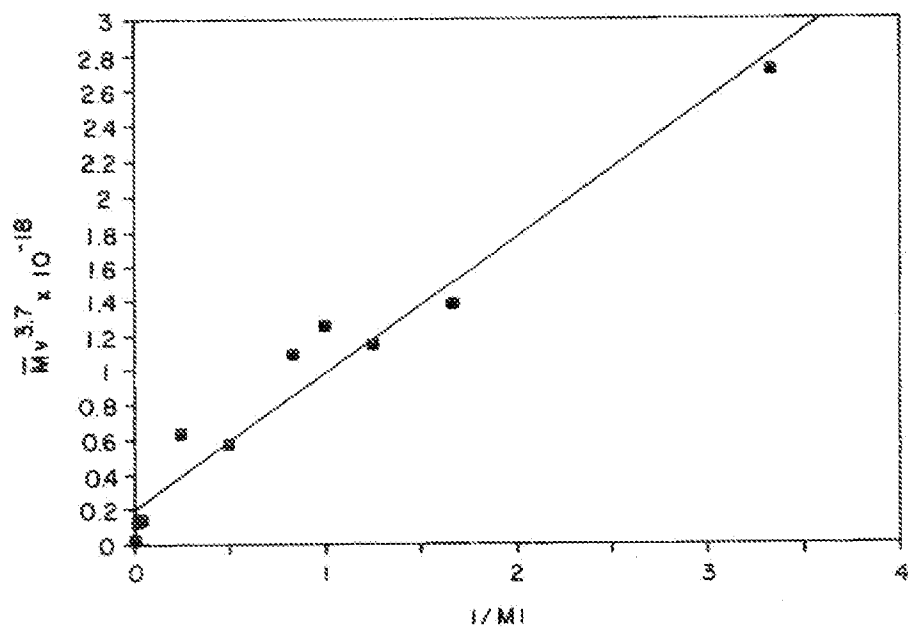


Fig. 4. Inverse melt flow index vs. $M_n^{0.37}$ for ethylene/1-butene copolymers.

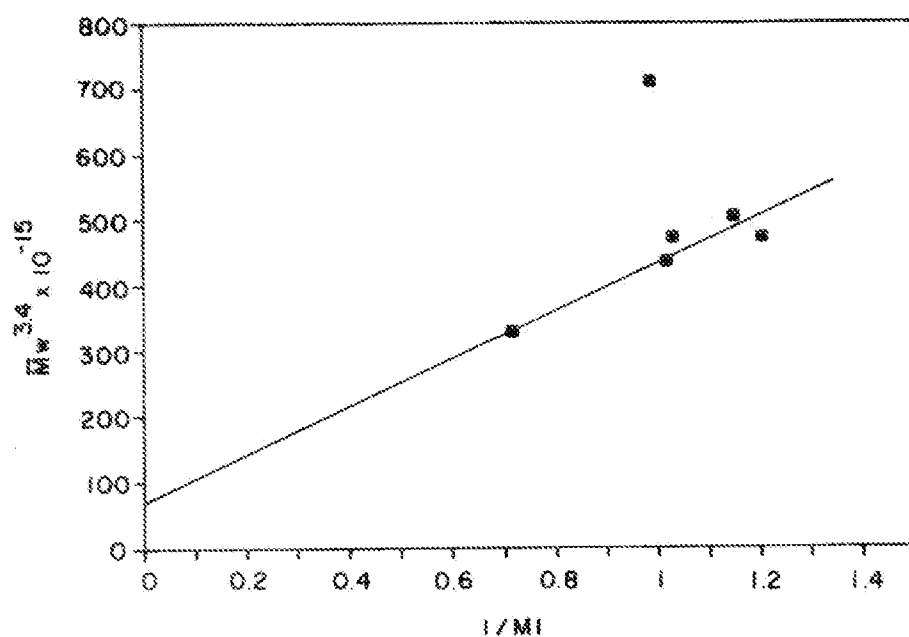


Fig. 5. Inverse melt flow index vs. $\bar{M}_w^{0.4}$ for ethylene/1-octene copolymers.

$$\bar{M}_w = -10332 \times \ln \text{MFI} + 76829 \quad (12)$$

with a correlation coefficient of 0.96. A reasonable correlation exists with the HDPE samples between $\ln \text{MFI}$ and \bar{M}_w . The data for this set of samples

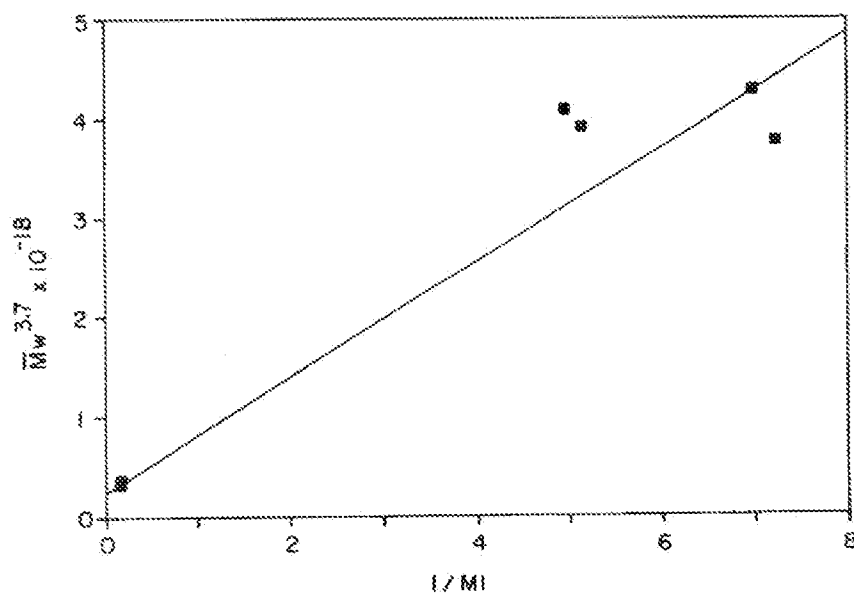


Fig. 6. Inverse melt flow index vs. $\bar{M}_w^{0.7}$ for HDPE samples.

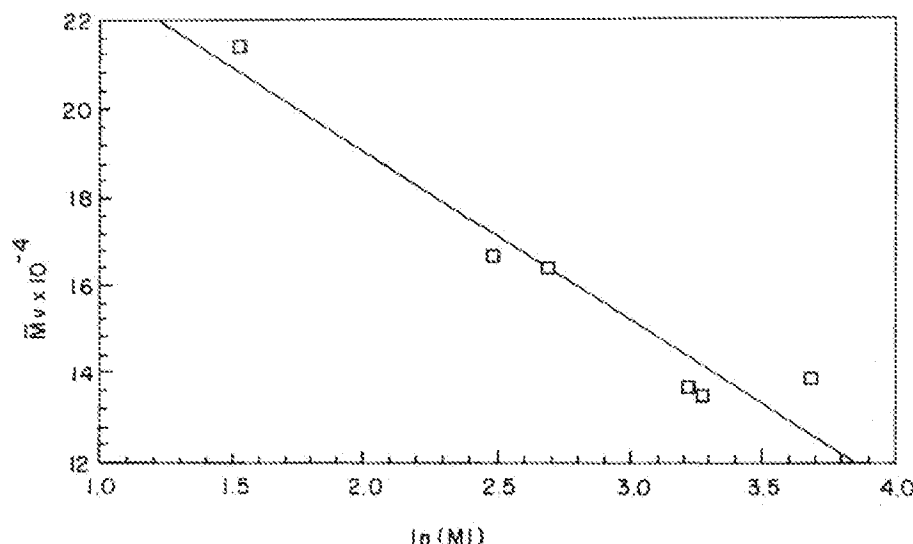


Fig. 7. $\ln(\text{melt flow index})$ vs. \bar{M}_n for polystyrene samples.

unfortunately have melt flow indices grouped at two relative extremes with no samples lying between. One could therefore argue that the correlation is not as significant as it could be with more intermediate data points. The equation of a linear fit to the $\ln \text{MFI}$ vs. \bar{M}_n data is

$$\bar{M}_n = -8480.6 \times \ln \text{MFI} + 62836 \quad (13)$$

with a correlation coefficient of 0.92.

The MFI probably reflects some undetermined features of the molecular weight distribution as well as the particular nature of intermolecular contacts between polymer molecules. For simplicity we may assume that the latter reflects entanglements in the usual sense. The relative influences of these two factors may vary between polymers. Commercial polystyrenes and polypropylenes¹⁷ have MWDs that are similar in shape. Their viscoelastic properties are relatively insensitive to shear history, indicating the existence of a constant entanglement network. The effects of shear history and variable entanglement states are more evident in the case of polyethylenes.⁷ Here the relation between MFI and \bar{M}_n is probably fortuitous for the particular samples we studied, since it is different for the butene LLDPEs and HDPEs and does not apply at all to the octene LLDPEs.

We believe, in conclusion, that the general analytical relation between MFI and \bar{M}_n or any other moment of the molecular weight distributions can be formulated and shown to have some validity for linear polymers of similar molecular polydispersity and processing history. For branched polymers, or for shear modifiable polymers, however, the situation is more complex and no general relationship will be obtained unless the rheological state of the polymer can be characterized.

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